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THERMOGRAVIMETRIC STUDIES OF NON-STOICHIOMETRIC CERIUM OXIDES UNDER ISOTHERMAL AND QUASI-ISOTHERMAL CONDITIONS

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Quasi-isothermal thermogravimetry is a new technique in which the programmed heating of a furnace automatically ceases when the rate of a reaction taking place in a sample, which is indicated by the DTG-signal, exceeds a preset limit. In this way reactions can be studied under nearly isothermal conditions. In this paper the data obtained using this method during oxidation and reduction experiments on non-stoichiometric cerium oxides are compared with the data obtained by conventional isothermal thermogravimetry. The kinetics of the composition changes during isothermal reduction and oxidation of CeO_{2-x} are also analyzed. It appears that, with some reservations, the experimental data are best described by the rate equation for a diffusion-controlled reaction. Finally, both the isothermal and the quasi-isothermal data suggest that the CeO_{2-x} phase region in the phase diagram consists of several subphases, each with a characteristic activation energy for the diffusion-controlled reactions.

Quasi-isothermal thermogravimetry is a new technique in which the continuous heating of the furnace is automatically stopped when the rate of a reaction taking place in the sample exceeds a preset limit. In this way the reaction takes place under nearly isothermal conditions and, as shown by Paulik and Paulik [1–3] who introduced this method, it gives a more accurate determination of the reaction temperature, more accurate kinetic data and a better separation of close-lying reactions than conventional non-isothermal thermogravimetry.

Previously, thermodynamic data for the non-stoichiometric cerium oxides (CeO_{2-x}) were determined using thermogravimetric measurements in atmospheres of controlled oxygen pressures under both isothermal and non-isothermal conditions [4–6]. The main purpose of these measurements was to establish equilibrium data for the system in order to construct an equilibrium phase diagram of the CeO_{2-x} phase range. The kinetics of the reactions taking place in the various non-stoichiometric and ordered phases discovered was therefore not considered in the previous work, and the purpose of the present study was to determine the kinetics of these reactions both under reducing and under oxidizing conditions. Two types of measurements were performed: (a) strictly isothermal measurements at various temperatures between 950° and 1450° in CO_2/CO atmospheres with a constant oxygen pressure throughout the reduction and the oxidation of the samples, and (b) quasi-isothermal thermogravimetric measurements in the temperature range

950 – 1530° in CO_2/CO atmospheres, the composition of which was varied during the experiment so that a constant oxygen pressure could be maintained during the heating of the sample. In this paper the data obtained in the strictly isothermal experiments are first examined in terms of different kinetic models, and it is shown that Jander's equation [7, 8] for diffusion-controlled reactions gives a good description of the data. Secondly, the data obtained from the quasi-isothermal thermogravimetric experiments are compared to those obtained from the strictly isothermal experiments, and it is shown that the two methods give comparable results.

Experimental

Quasi-isothermal thermogravimetric experiments

An electronic regulator for quasi-isothermal analysis (QIA) was developed for the Netzsch Simultaneous Thermoanalyzer used in this investigation. As shown in Fig. 1, the principle of this method is as follows: When the sample during the programmed heating reaches the reaction temperature and a deviation in the weight curve is obtained, a DTG-signal proportional to the slope of the weight curve will also be produced in the DTG-amplifier. With the regulator two limits can be preset for the DTG-signal and, as shown in the Figure, the heating of the sample ceases when the DTG-signal passes the upper limit, whereas the heating is resumed when the DTG-signal passes the lower limit when the reaction is nearly completed. Two different types of behaviour can be envisaged using this method:

(1) If the rate of the reaction taking place in the sample is so large that the DTG-signal remains outside the preset limits during the whole reaction period, there will be strictly isothermal conditions and the weight curve will have the sigmoid form shown in Fig. 1.

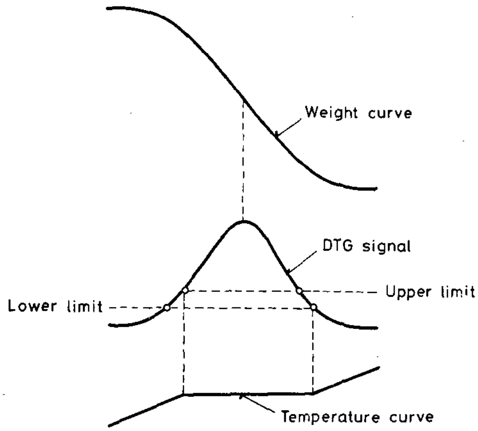

Fig. 1. Principle of quasi-isothermal analysis

(2) If only a small portion of the sample reacts when the reaction temperature is reached, the DTG-signal will quickly return to the lower preset limit, the heating will be resumed and a small portion of the sample will react again, etc. This will cause the DTG-signal to fluctuate between the two limits and the weight curve obtained in this case will be a straight line. The sample will only be heated a few degrees during each step and the reaction will take place under quasi-isothermal conditions.

The following conditions were used in the quasi-isothermal experiments performed on CeO_{2-x}:

Temperature range: 950 – 1550°. Heating rate: 10°/min. Atmospheres: CO_2/CO mixtures. Oxygen pressure: $-\log pO_2$: 10.25 and 11.95. Sensitivities: TG 1 – 5 mg/cm; TG2 – 0.5 mg/cm; DTG – 0.16 mg/min · cm.

The reaction rate for the reductions and oxidations taking place with increasing temperature in the various non-stoichiometric and ordered phases existing in the CeO_{2-x} system [5, 6] undoubtedly depends on the oxygen pressure in the atmosphere. In order to keep this parameter constant during the experiment, the CO_2/CO ratio was varied in a precalculated manner as the temperature of the sample increased. After each change of the CO_2/CO ratio, the composition of the atmosphere was checked with a gas-chromatograph.

Isothermal experiments

The isothermal reduction and oxidation experiments on CeO_{2-x} were also performed in the Netzsch Simultaneous Thermoanalyzer. The following conditions were used:

Temperatures: 950, 1050, 1150, 1250, 1350 and 1450°. Atmospheres: Reduction: $CO_2/CO \simeq 0.04/0.85$ (1050°, experiment no.2); Oxidation: $CO_2/CO \simeq 28$. Sensitivities: TG 1 – 5 mg/cm; TG 2 – 0.5 mg/cm; DTG – 0.16 mg/min · cm.

In these measurements the sample was heated to the reaction temperature in the strongly oxidizing atmosphere used in the oxidation experiments. After equilibration in this atmosphere, the CO_2/CO ratio was changed to the ratio used in the reduction experiments and after a short delay of 2 – 3 min the reduction of the sample started. When the reduction was complete, as indicated by the return of the DTG-signal to its baseline, the composition of the atmosphere was again changed to the CO_2/CO ratio used in the oxidation experiments and after a short delay the sample started again to oxidize. Finally, after the oxidation was completed the sample was heated to the next reaction temperature and the reduction and oxidation experiments were repeated.

Evaluation of isothermal data

According to many text books on reaction kinetics and thermal analysis – see, for instance, references [8 – 10] – a kinetic equation exists between the reacted fraction (α) and the time (t) for a heterogeneous reaction under strictly isothermal conditions. The form of this equation depends on the type of rate-limiting process that controls the overall reaction and which is the slowest process. Table 1 shows the kinetic equations when the rate-limiting process is diffusion, and when it is a reaction at the phase boundary between the reactant and the reaction product.

Table 1

Kinetic equations for rate-limiting processes

Rate-limiting process	Equation*	References
1. Diffusion — three-dimensional, spherical symmetry; Jander's equation	$F(\alpha) = (1-(1-\alpha)^{1/3})^2 = (k/r^2)t$	7
2. Phase boundary movement with constant velocity, u-spherical symmetry	$F(\alpha) = (1-(1-\alpha)^{1/3}) = (u/r)t$	11, 12

* In these equations r is the particle radius and k is a constant

The composition of the sample, $(2-x)$ in CeO_{2-x}, was calculated as a function of time from the isothermal weight curves obtained using the equation

$$2 - x = \frac{W_S \cdot M_{\mathrm{ClO}_2}}{W_{\mathrm{CeO}_2} \cdot 16} - \frac{M_{\mathrm{Ce}}}{16} = W_S \cdot k_1 - k_2$$

where W_S represents the weight of the sample at time t, W_{CeO_2} the weight of the sample in the stoichiometric reference state, M_{CeO_2} and M_{Ce} the molecular weights of CeO_2 and Ce, respectively, and k_1 and k_2 the constants that can be calculated after W_{CeO_2} has been determined. The fraction reacted at a given time was calculated from

$$\alpha = \frac{(2-x)_t - (2-x)_0}{(2-x)_\infty - (2-x)_0}$$

where $(2-x)_t$, $(2-x)_0$ and $(2-x)_\infty$ are the composition of the sample at times t, 0 and ∞, respectively. All calculations were performed on a programmable desk calculator, which was also programmed to calculate in the same run the $F(\alpha)$ values for the two kinetic equations shown in the Table.

The type of rate-limiting process was evaluated as follows: Considering the form of the equations shown in the Table it is evident that only the actual rate-limiting process will give a linear relationship when $F(\alpha)$ is plotted as a function of time. The two $F(\alpha)$ values calculated from the experimental data were therefore plotted in this manner and the appearance of straight lines in these plots was considered as an indication of the type of process governing the reactions taking place during the reductions and oxidations of the sample.

Results and discussion

Isothermal experiments

Figure 2 shows the experimental weight and DTG-curves plotted on the recorder during the 1450° reduction and oxidation experiments. From the figure it will be noted that there is a short delay after the composition of the atmosphere has been changed, but that the reduction of oxidation then takes place very rapidly. At the beginning of the process the slope of the weight curves is very large and a large DTG-signal, which is difficult to evaluate in detail, is obtained. During the last part of the process, however, the rate becomes smaller and the DTG-signal gradually approaches its baseline. If the same phase exists in the sample during the whole reaction period, the DTG-signal would be expected to follow an exponential curve during its decay towards its baseline, but as shown in Fig. 2, this is not the case. After about 20 min, the DTG-signal slightly increases in the reduction experiment, and this can perhaps be taken as an indication of a phase change – a new phase is formed with another activation energy, and thus another reaction rate. Although the phase changes indicated in this way in some cases correspond to the phase changes seen in previous studies [6], the significance of the DTG-signal must be examined in greater detail before these indications can be fully interpreted.

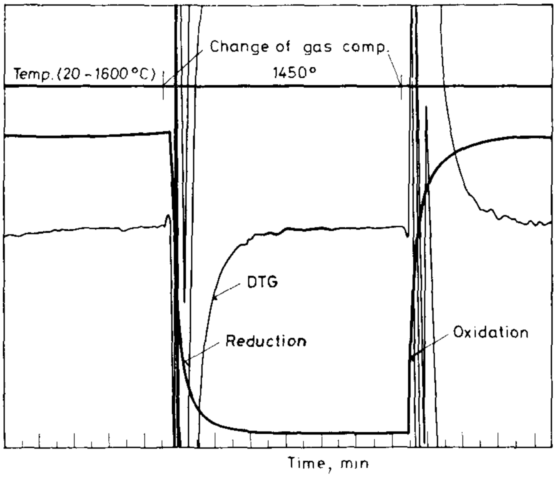

Fig. 2. Isothermal experiment: CeO_{2-x} in CO_2/CO

The $F(\alpha)$ values calculated from the weight curves shown in Fig. 2, as well as from the weight curves obtained in the other isothermal experiments, were all plotted as a function of time as described in the previous section. Only the $F(\alpha) = (1 - (1 - \alpha)^{1/3})^2$ *vs.* t plot gave a linear relationship, however, and the data thus suggest that the reactions are diffusion-controlled. Figure 3 shows the lines obtained in this plot for the 950 and 1050° experiments as an example.

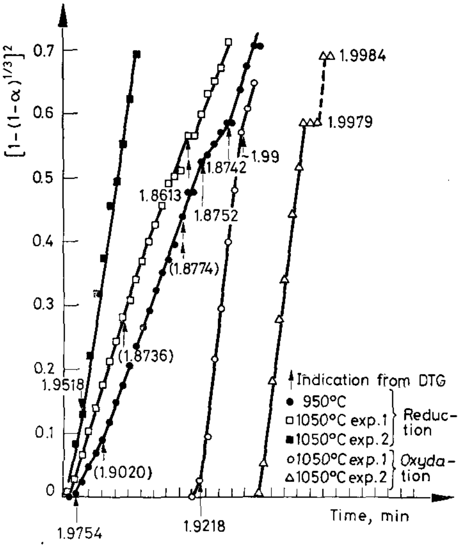

Fig. 3. $F(\alpha)$ for diffusion-controlled reactions as a function of time for reduction and oxidation experiments at 950 and 1050°

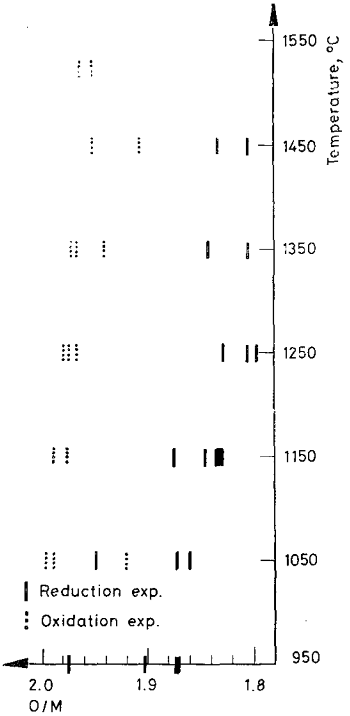

Fig. 4. Phase limits indicated in isothermal reduction and oxidation experiments

From Fig. 3 it is also evident that the same linear relationship cannot describe all the data obtained in a given experiment. At certain compositions the slope of the lines changes, indicating the formation of new phases with other activation energies for the diffusion. If the compositions found for the breaks in the lines in all the experiments performed are plotted as a function of temperature, the diagram shown in Fig. 4 is obtained. Each marking in this diagram corresponds to a phase change in the system, and the results obtained in this investigation thus support the results obtained in previous investigations [6], which indicated that the CeO_{2-x} phase consists of several subphases and not just of a single, grossly non-stoichiometric phase. Some of the phase limits shown in Fig. 4 correspond closely to the phase limits found previously, whereas others do not, and more detailed kinetic studies are necessary before a final phase diagram for CeO_{2-x} can be drawn.

The conclusion that the reactions in this system are diffusion-controlled must also be taken with some reservation as the possibility of other rate-limiting processes – nucleation for instance – has not yet been fully explored. It is certain, however, that the experimental data obtained in this work are much better described by the equation for diffusion-controlled reactions than by the equation for phase-boundary-controlled reactions, in contrast to the conclusion of Hyde et al. [13] from their studies of the oxidation kinetics of PrO_{2-x}, which is a similar oxide system, that the reactions are phase-boundary-controlled over a part of the composition range.

Quasi-isothermal experiments

An example of the curves recorded during the quasi-isothermal experiments on CeO_{2-x} is shown in Fig. 5. It will be noted that the temperature in this type of measurement varies stepwise and that the sample weight, and thus the oxygen content of the sample, decreases at each step, producing a corresponding DTG-peak. Disregarding the fluctuations in the DTG-curve resulting from changes in atmosphere made in order to keep the oxygen pressure constant during the experiment, as explained in the previous sections, it will further be noted that the height of the DTG-peaks varies in a systematic manner. Tentatively, this is explained in the following way: Previous studies [6] have shown that the CeO_{2-x} phase range can be divided into several subphases each having a characteristic activation energy for the diffusion-controlled reductions, as indicated by the isothermal kinetic studies described in the previous section. When the composition of the sample is changed so that a new subphase is formed, a large proportion of this new phase is transformed already at the first temperature level encountered and a large DTG-peak must be expected for this temperature level. A smaller amount of this phase is now available for the transformation at the next temperature level and the height of the second DTG-peak must therefore be smaller than for the first and vice versa. As long as the phase still remains unchanged, the DTG-peak heights will thus decrease for each temperature level, probably in an exponential way. If the experi-

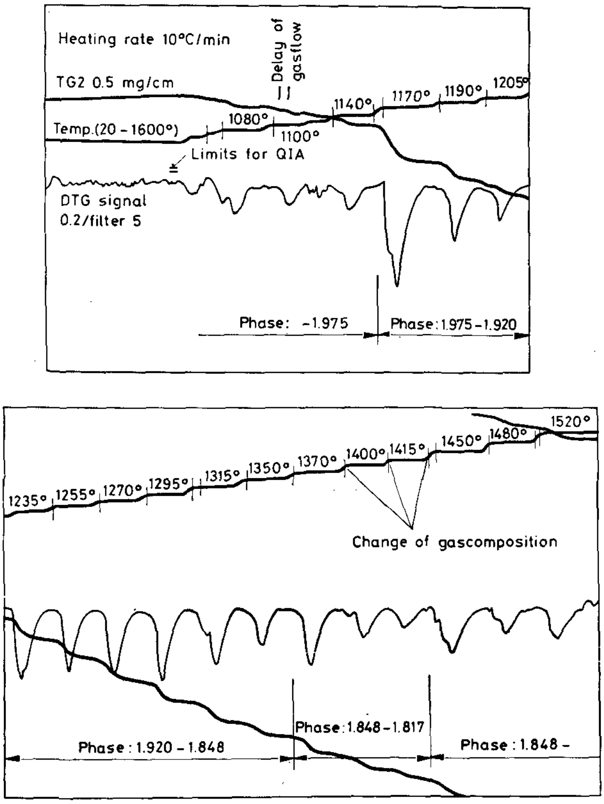

Fig. 5. QIA experiment: CeO_{2-x} in CO_2/CO, with $\log pO_2 = -10.25$

mental curves shown in Fig. 5 are interpreted in this way, the phase limits shown in the Figure are obtained and if these are compared with the limits found in the isothermal experiment (see Fig. 4) it is clear that the two methods gives comparable results.

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Résumé — La thermogravimétrie quasi-isotherme est une technique nouvelle dans laquelle le chauffage programmé d'un four cesse automatiquement dès que la vitesse d'une réaction au sein de l'échantillon, indiquée par le signal TGD, dépasse une limite préalablement établie. On peut ainsi étudier des réactions en conditions sensiblement isothermes. Dans cet article, les données obtenues par cette méthode, lors d'expériences d'oxydation et de réduction d'oxydes non stœchiométriques du cérium sont comparées à celles obtenues par thermogravimétrie isotherme conventionnelle. La cinétique des changements de composition au cours de la réduction et de l'oxydation de CeO_{2-x} est également étudiée. Sous certaines réserves, il semble que les données expérimentales sont mieux décrites par une équation où la vitesse de réaction est contrôlée par la diffusion. Enfin, les données obtenues en régimes isotherme et quasi-isotherme suggèrent que, dans le diagramme de phases, le domaine de la phase CeO_{2-x} consiste en plusieurs sous-phases, chacune possédant une énergie d'activation caractéristique de réactions contrôlées par diffusion.

Zusammenfassung — Die quasi-isotherme Thermogravimetrie ist eine neue Technik, be welcher die programmierte Heizung eines Ofens automatisch aufhört, sobald die Reaktionsgeschwindigkeit in der Probe, registriert durch das DTG-Signal, eine im vorhinein bestimmte Grenze überschreitet. Auf diese Weise können Reaktionen unter beinahe isothermen Bedingungen untersucht werden. In dieser Veröffentlichung werden die durch diese Methode während der Oxidations- und Reduktionsexperimente an nicht-stöchiometrischen Ceroxiden erhaltenen Angaben mit jenen verglichen, welche durch konventionelle isotherme Thermogravimetrie erhalten wurden. Die Kinetik der Änderungen in der Zusammensetzung während der isothermen Reduktion und Oxidaten von CeO_{2-x} wurde ebenfalls analysiert. Es scheint, dass mit einigem Vorbehalt, die Versuchsdaten am besten durch die Geschwindigkeitsgleichung einer diffusiongesteuerten Reaktion beschrieben werden können. Sowohl die isothermen als auch die quasi-isothermen Daten gestatten den Schluss, dass die Umgebung der CeO_{2-x} Phase im Phasendiagramm aus mehreren Unterphasen besteht, mit jeweils charakteristische Aktivierungsenergien für die diffusionsbedingten Reaktionen.

Резюме — Квази-изотермическая термогравиметрия является новой техникой, в которой печь с программным нагревом автоматически отключается, когда скорость реакции, протекающей в образце и показываемой ДТГ сигналом, превышает данный предел. Таким путем реакции могут быть изучены при почти изотермических условиях. В настоящей статье данные, полученные при использовании этого метода в реакциях окисления и восстановления нестехиометрических окислов церия, сопоставлены с даиными, полученными обычной изотермической термогравиметрией. Проанализирована кинетика изменений состава во время изотермического восстановления и окисления CeO_{2-x}. Кажется, с некоторыми оговорками, что экспериментальные данные наилучше огисываются уравнением скорости диффузионно-контролируемой реакции. В конце концов изотермические и квази-изотермические данные предполагают, что фазовая область CeO_{2-x} на фазовой диаграмме состоит из нескольких субфаз, каждая с характерной энергией активации для диффузионно-контролируемых реакций.